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by

R. Ramanathan, J.A. Zimmerman, and J.R. Eyler

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Ionization Potentials of Small Carbon Clusters

Ragulan Ramanathan, Jeffrey A. Zimmerman[†] and John R. Eyler
Department of Chemistry, University of Florida
Gainesville, Florida 32611-2046

[†]Present address: IBM Technology Laboratory, Dept T37, P.O.Box 8003, Endicott, NY 13760-5553.

ABSTRACT

Ionization potentials (IP's) of small carbon clusters (C_n, n=3-6) have been bracketed with an uncertainty of a few tenths of an eV by charge-transfer methods in a Fourier transform ion cyclotron resonance mass spectrometer. Values obtained are compared to previously determined experimental and theoretical values. Several interesting reactions other than charge-transfer were observed between the carbon cluster ions and the charge-transfer reference compounds. The products of these reactions are reported and discussed.

INTRODUCTION

The growing number of recent publications on carbon clusters shows the tremendous interest in this class of compounds. Some earlier studies have shown that cluster configuration and reactivity differ from those of the bulk.[1,2] Knowledge of chemical and the physical properties of small carbon clusters can serve as a bridge to understanding the behavior of larger carbon clusters and the bulk. In addition, small carbon clusters have been of particular interest because of their importance in combustion processes, interstellar space and comet tails.[3]

Theoretical investigations of small carbon clusters have involved ab initio calculations of both electronic states and geometric structures. The pioneering ab initio calculations by Pitzer and Clementi[4] on small carbon clusters predicted that for linear C_n chains the odd-numbered clusters are more stable than the even-numbered clusters, and the odd-numbered C_n are in singlet ground states while the even-numbered C_n are in triplet ground states. The enhanced stability of the odd-numbered carbon clusters was postulated to be due to completely filled π molecular orbitals. These theoretical findings by Pitzer and Clementi were later supported experimentally by Weltner and co-workers[5] and theoretically by Ewing and Pfeiffer.[6] Pitzer et al. expanded their semiempirical calculations to even-numbered rings and predicted that a transition from more stable odd-numbered linear chains to even-numbered monocyclic rings should occur around C_{10}.[7] In addition, self-consistent Modified Neglect of Differential Overlap (MNDO) calculations by Bernholc and Phillips predicted stable neutral rings for C_n, n = 10, 14, 18 and 22 and stable C_n^+ for n = 11, 15, 19 and 23.[8]

A review by Weltner and Van Zee has summarized experimental and theoretical studies of small carbon clusters through November 1988.[9] Since then, several new experiments have contributed to our knowledge of small carbon clusters, including definitive IR-spectroscopic characterization of C_3, C_4 and C_5 and observation of the IR spectrum of C_3 and C_5 in a carbon star.[10-16] The primary goal of many earlier studies was to follow changes in the cluster chemical and physical properties as the number of carbon atoms was varied. Though carbon clusters as large as 600 atoms have been studied experimentally[17], little detailed experimental information is available for small carbon clusters.

The ionization potential (IP) of a cluster is one of its most important physical properties. Accurate determination of the ionization potentials of small carbon clusters can lead to a better understanding of their reactivity and configuration. Previously, Rohlfing and co-workers have determined the ionization potentials of carbon clusters by laser photoionization of neutral clusters to produce positive cluster ions.[18] The ionization potentials determined by laser photoionization are vertical rather than adiabatic[19] and the earlier work also led to quite "coarse" brackets.

Laser desorption FTICR (LDFTICR) studies of carbon cluster ion reactivity have provided information about the presence of differing isomeric forms of carbon clusters and indirect information about structures.[20-23] These studies have also indicated that LDFTICR mass spectrometry is an ideal technique for studying the reactivity and the structure of cluster ions. The ionization potentials determined by FTICR reactivity studies are expected to be closer to adiabatic than vertical. Carbon cluster ions are

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formed directly in the cell by laser desorption of a graphite plug. Once the C_n^+ of interest is trapped in the cell, during a "thermalizing" period it undergoes many ion-molecule collisions (≥ 100) with the thermalizing gas and loses most of its internal energy. Charge-transfer reactions between the cluster ions and neutrals of known IP are then monitored.[23-26] If reaction occurs, it is expected that the long lifetimes of the charge-transfer ion-molecule complexes will allow for geometry changes from the most stable ionic structure to the most stable neutral structure. Since the ionization potentials determined by the FTICR experiments are not corrected to 0 K for the ions and neutrals involved, the ionization potentials determined are not true adiabatic values, but should approach them quite closely.[26]

Ionization potentials of carbon clusters containing from 6 to 24 atoms and from 48 to 200 atoms have been bracketed with an uncertainty of few tenths of an eV using the charge-transfer bracketing technique.[23-24] This method has also proven valuable in determining the ionization potentials of arsenic, phosphorus and coinage metal clusters.[25-26]

In this study, the charge-transfer bracketing method was used to determine the IP's of carbon clusters containing from 3 to 6 atoms. The uncertainties assigned to the IP's ($\pm$ a few tenths of an eV) are substantially less than those reported earlier.

EXPERIMENTAL

All experiments were performed using a home-built FTICR mass spectrometer equipped with a Nicolet[27] FTMS 1000 data station, prototype 2 Tesla superconducting magnet, and a heated inlet system equipped with two precision leak valves. The high

vacuum chamber (15.2 cm inside diameter and 1 meter long) was pumped by two oil diffusion pumps(15 cm and 10 cm diameter).[28] A third diffusion pump[28] with a pumping speed of 300 L/s was mainly used for initial pump down of the system and to pump on the inlet system. A combined pumping speed of 1000 L/s of the high vacuum chamber diffusion pumps and baking at 100 °C overnight maintained the background pressure of the system at 2×10^{-9} Torr. (Pressures were measured with an (uncorrected) ionization gauge. Although a detailed study of rate coefficients, such as reported in References 25 and 26, was not made in this case, comparable rates of reaction (with k's ranging from the mid 10^{-10} to low 10^{-9} cm^3/s) were found for selected reactions.) The high vacuum chamber was mounted inside the 20 cm bore of the superconducting magnet. This system was equipped with three laser windows on the 8 inch cell flange and two laser windows on the 6 inch solids probe inlet flange.

A stainless steel cell (2.5x2.5x4.5 cm) was used in all charge transfer reaction studies. A trapping potential of 2.0 V was used in all experiments. The cell trapping plates were each made with a 2 cm diameter hole over which 90% transparent stainless steel mesh was spot welded to maintain the required trapping potential. The carbon clusters were produced by focusing (7.63 cm focal length quartz lens) the fundamental (1064 nm) output of a Nd:YAG laser through the front and back trap plates onto a graphite plug mounted behind the back trap plate of the cell. In order to synchronize the Nicolet console and the Nd:YAG laser electronically, the total pulse sequence time was maintained as a multiple of 226.3 ms. A home-built microcomputer interface allowed the laser Q-switch to be triggered on every other firing of the flashlamps.[29] The

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laser was fired with an energy of 5-15 mJ/pulse, measured by means of a power/energy meter placed in front of the quartz window through which laser irradiation entered the FTICR vacuum chamber. The area of the focused laser beam was 0.1 mm^2.

The pulse sequence used in this experiment has been explained in detail.[23] A quench pulse was first applied to both trap plates to eject any ions present in the cell, followed by a variable quench delay time which allowed remaining collision gas to be pumped away. The laser was then triggered and a pulsed valve[30] was opened briefly to admit argon into the vacuum chamber (peak pressure 6.6 x 10^{-6} Torr). Next, a 900 ms delay time allowed the ions to be thermalized by ion-neutral collisions with argon. During this delay time most of the thermalizing gas was also pumped from the vacuum chamber. A series of ion ejection sweeps was then used to isolate the cluster cation of interest. After the cluster ion was isolated, a variable reaction time allowed the charge-transfer reaction to take place. Ions were excited by the standard frequency chirp excitation method, and 16K time-domain points were acquired during broad-band detection (25-400 amu).

For each reaction delay time, fifty scans were averaged to enhance the signal-to-noise ratio. The intensities of the reacting cluster ion and product ions formed by ion-molecule reaction(s) were followed for a time period which ranged from 1 to 10 s. Integrated peak intensities for all major ions were obtained at 15 to 20 different reaction delay periods of approximately equal spacing during each experiment. Plots of relative ion intensities vs. reaction time were then made to demonstrate the occurrence or non-occurrence of charge transfer reactions.

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The charge-transfer reagents, listed in Table 1, were introduced into the vacuum chamber usually to a pressure of 1-3 x 10^{-8} Torr above the background pressure. If the charge-transfer reaction was not observed at these low pressures, the neutral pressure was increased to 1.0 x 10^{-7} Torr to further confirm the occurrence or non-occurrence of reaction. The charge-transfer reference gases were obtained from commercial sources and used without further purification. However, liquid reference compounds were purified by several freeze-pump-thaw cycles and tubes containing the solid reference compounds were evacuated for 1-2 minutes before the vapor from the compounds was admitted into the vacuum chamber.

RESULTS

Mass spectra are shown in Figures 1a and 1b for carbon cluster cations formed from the graphite rod by laser desorption. Two different pulse energies were used at the fundamental wavelength of the Nd:YAG laser. Comparison of these mass spectra indicates that the cluster ion distribution depends on the laser energy. Figure 1a shows the cluster distribution obtained with 5 mJ/pulse of laser energy; intense peaks (decreasing intensity) were observed for C_{11}^+, C_{15}^+, C_{10}^+, C_{14}^+, C_{12}^+, C_7^+ C_{19}^+, C_{18}^+, C_{16}^+ and C_3^+. Increasing the laser energy to 15 mJ/pulse caused the cluster distribution to shift as shown in Figure 1b. At this laser energy intense peaks were observed for C_{11}^+, C_7^+, C_3^+, C_5^+, C_{15}^+ and C_{19}^+.

Results of charge transfer reactions between C_n^+ and neutral reference compounds are listed in Table 2. The ionization potential for each carbon cluster reported in Table 3 was taken as the value midway between the ionization potentials of

neutrals for which charge-transfer was and was not observed. For example, C_3^+ did undergo charge-transfer with nitrous oxide(12.89 eV) but did not charge-transfer with sulfuryl fluoride(13.04 eV). Since the IP of C_3 can lie anywhere between 12.89 and 13.04 eV, the uncertainty is reported as $\pm \frac{1}{2}$ the gap size. In this particular case, the gap is 0.15 eV, giving an uncertainty of 0.075 eV for C_3 (rounded to 0.1 eV in Table 3).

Typical plots of normalized ion intensities vs. reaction time for C_3^+ with xenon are shown in Figure 2. Plots similar to these were obtained for C_4^+ and C_5^+. Since the C_n^+ intensity decreases exponentially to zero, these curves suggest that only one form of each C_n^+ is being produced by laser desorption of the graphite plug. All six major isotopes were observed for xenon and the sum of these intensities was used as the xenon ion intensity in these plots.

Xenon and krypton were the only reference compounds which did not react via non-charge-transfer reactions with small carbon clusters. Figures 3a, 3b and 3c show the charge-transfer reaction and the side reactions observed for C_3^+, C_4^+ and C_5^+, respectively, reacting with N_2O. As shown in these figures only C_3^+ undergoes a charge-transfer reaction with N_2O. Since the normalized intensity of N_2O^+ did not exceed 25% of the zero-time normalized intensity of C_4^+, C_5^+ or C_6^+, we have attributed no charge-transfer to these reactions. This rule was applied throughout this study.

Table 3 compares the ionization potentials determined in this study with some previously reported experimental and theoretical values. Several ion-molecule reactions were observed in addition to charge-transfer reactions. Although these ion-molecule reactions caused some difficulties in bracketing the IP's of small carbon clusters, they

gave some insight into the reactivity of small carbon clusters. Some of these ion-molecule reactions are reported in Table 4.

DISCUSSION

a) Carbon Cluster Distribution:

The cluster ion distributions obtained by direct laser ablation of a graphite plug are shown in Figures 1a and 1b. These spectra show that cluster ions with 3, 7, 10, 11, 12, 14, 15, and 19 atoms are formed in high abundance. A similar distribution was observed in previous studies using different lasers.[18,23,31] Ionization potentials determined earlier by the charge-transfer bracketing technique for C_n (n=6-24) showed that clusters with 7, 11, 15, 19 and 23(4n+3) atoms (n=1-5) exhibited IP's lower than those of neighboring clusters.[23] It was also suggested that clusters of these sizes(7, 11, 15, 19 and 23) may not possess any special stability, but rather are simply more easy to ionize because of their lower IP's. It was suspected that this trend might also extend to C_3. The cluster ion distribution does show a high abundance of C_3^+. However, the IP bracketed in this work for C_3 (12.97±0.1 eV) is higher than that of its neighbors C_4 (12.54±0.35 eV) and C_2 (12.0±0.6 eV[32], 12.15±0.05 eV[33], 9.98-11.61 eV[18], 11.09 eV[34], 12.16 eV[34], 11.78 eV[35], 11.85 eV[35], 12.51 eV[35] and 12.60 eV[35]). This suggests that the trend observed for other clusters with 4n+3 atoms does not hold for the n=0 case.

Our attempts to bracket the IP of C_2 were not successful due to the low abundance of C_2^+ produced by laser desorption from the graphite plug. This ion also reacted via non-charge-transfer pathways with most of the charge-transfer reference compounds. In one series of experiments the trapping potential was dropped to a value

between 0 and 1 volts during the laser desorption time period in an attempt to allow ions (perhaps C_2^+) with low kinetic energy to enter the FTICR cell. The potential was returned to 2 volts before the subsequent thermalization and reaction period. However, this approach did not enhance the abundance of C_2^+, although it did change the distribution of the carbon cluster cations somewhat. Thus a constant trapping potential of 2 Volts was used for all experiments reported here.

b) Ionization Potentials:

Table 3 compares the ionization potentials obtained in this study with some previously reported experimental and theoretical values. Although IP's have been bracketed in a reliable straightforward manner by the charge-transfer technique in the past, some limitations are attached to this technique, especially with the small carbon clusters studied in this work: (i) Reactions other than charge-transfer often occur between small carbon cluster ions and most of the charge-transfer reference compounds. These reactions usually cause larger IP uncertainties by increasing the gap between the reference compounds for which charge-transfer clearly does and does not occur. For example, because of its reactions (other than charge-transfer) with freon-13 and sulfur dioxide, a gap of this nature of 0.70 eV for C_4 makes the uncertainty of its IP ±0.35 eV. (ii) Fewer suitable charge-transfer reference compounds are available to determine the higher IP's of the small carbon clusters. This again leads to a larger gap between the IP's of reference compounds which do and do not undergo charge-transfer, and thus to a larger stated uncertainty. (iii) Carbon cluster ions may be thermalized incompletely before the charge-transfer reaction time period. For the

bracketing technique to be valid, cluster ions which undergo charge-transfer should be in the lowest energy forms produced by the laser and should be cooled by numerous ion-molecule collisions with the neutral thermalizing gas(argon). If complete thermalization were not achieved the bracketed IP would be higher than the actual IP. Such thermalization depends on the thermalizing time, the molecular complexity and the pressure of the thermalizing gas. A thermalizing time of 900 ms and peak pressure of 6.6×10^{-6} Torr argon were used in these experiments. For each of the bracketed IP's, the charge-transfer reactions which determined the upper and the lower boundaries were studied with and without the thermalizing gas. The occurrence of these reactions showed no dependence on the introduction of the thermalizing gas; however, their rates often did. For example, when benzene was used as a charge-transfer reference compound without thermalizing gas, the charge-transfer between C_4^+ and C_6H_6 was 85% complete at a reaction time of 680 ms, but the corresponding reaction time increased to 1130 ms when the thermalizing gas was introduced.

IP of C_3

The IP bracketed by the charge-transfer technique for C_3 (12.97±0.1 eV) is in generally poor agreement with previous theoretical (11.5 eV[35]) and experimental (9.98-11.61 eV[18] and 11.1±0.5 eV[37]) vertical IP's. The theoretical IP of 11.5 eV for C_3 was calculated using multiconfiguration self-consistent field (MC-SCF) theory. The experimental IP between 9.98 eV and 11.61 eV was bracketed using photoionization time-of-flight mass spectrometric techniques. The IP of 11.1±0.5 eV for C_3 was determined in carbon vapor produced by sublimation of graphite, employing a Knudsen cell and a double-focusing mass spectrometer.

The adiabatic ionization potential calculated for C_3 using all-electron *ab initio* molecular orbital theory is 11.4 eV.[38] This value is 1.57 eV lower than the IP bracketed in this study, but the present value (12.97±0.1) is in good agreement with some of the previous theoretical (12.7 eV[39] and 12.95 eV[40]) and experimental (12.6±0.6 eV[32] and 12.1±0.3 eV[41]) determinations of the IP's for C_3. The IP of 12.7 eV for C_3 was calculated using the equations of motion method and the IP of 12.95 eV was calculated using the multireference double excitation configuration interaction (MRD CI) method. IP's of 12.6±0.6 eV and 12.1±0.3 eV were both determined by a Knudsen cell double-focusing mass spectrometer, using carbon vapor produced by sublimation of graphite. The IP (12.97±0.1) bracketed in this study falls within previously determined IP[32,39-41] ranges for C_3 and the uncertainty has been reduced to 0.1 eV.

IP of C_4

The existing literature value for the IP of C_4 (12.6 eV[32]) was obtained using carbon vapor produced from sublimation of graphite ($C_4 \longrightarrow C_4^+ + e$). This agrees very well with the IP value (12.54±0.35 eV) bracketed in this study for C_4. However, our IP agrees poorly with the adiabatic IP (10.58 eV) calculated by Raghavachari and Binkley.[38] Also, our IP does not agree with the vertical IP bracketed (9.98-11.61 eV[18]) using the PI-TOF-MS technique. The IP (12.54±0.35 eV) bracketed here has less uncertainty than the IP determined by the PI-TOF-MS technique, and given the difficulties in determining the thresholds for three-and four-photon processes, should be more accurate as well.

IP of C_5

The IP of 12.26±0.1 eV bracketed for C_5 by our FTICR method is 0.24 eV lower

than the IP (12.5 ± 0.1 eV[32]) determined previously by using carbon vapor produced from sublimation of graphite ($C_5 \text{----}> C_5^+ + e$) and a Knudsen cell double-focusing mass spectrometer. However, the IP reported here is slightly higher than the vertical IP obtained in a PI-TOF-MS study (9.98-11.61 eV[18]). Also, it is in poor agreement with the adiabatic IP (10.7 eV) calculated by Raghavachari and Binkley.[38]

IP of C_6

The IP (9.70 ± 0.2) of C_6 reported here agrees very well with the IP of C_6 previously determined by our group using the same technique but with a different laser and different reference compounds.[23] The IP bracketed here is also in good agreement with the adiabatic IP (9.8 eV) calculated using the all-electron *ab initio* molecular orbital theory.[38] In addition to this, our IP for C_6 is slightly lower than the vertical IP (9.98-11.61 eV) bracketed using the PI-TOF-MS technique.[18]

In addition to the above results, studies by Knight *et al.*[42] and McElvany[21] roughly estimated the IP's of small carbon clusters using FTICR methods. Knight *et al.* suggested that carbon clusters, C_n, $n\le10$, have IP's greater than 9.9 eV and $n>10$ have IP's lower than 9.9 eV. This estimation was based on a reaction between laser-generated carbon cluster cations and C_6H_{12}. Carbon cluster cations C_n^+, $n\le10$, did, and $n>10$ did not, undergo charge-transfer with C_6H_{12}. This estimation by Knight *et al.* agrees well with our IP's for C_3 to C_6, but agrees poorly with the IP's bracketed[23] for C_7 through C_{10}. McElvany[21] observed C_n^+ with $n=3-5$ to undergo charge-transfer with ethylene (10.45 eV) and C_n^+ with $n>5$ not to undergo charge-transfer with ethylene. This allowed McElvany to place the IP's of carbon clusters, C_n, $n=3-5$, greater than

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10.45 eV and the IP's of C_n, n>5 less than 10.45 eV. This estimation agrees very well with the IP's bracketed in this study and in previous work in this laboratory.[23]

Although most of the recent mass spectrometric studies of carbon cluster ions have involved formation of carbon clusters from laser desorption of graphite[20-23,42] carbon cluster ions have also been produced from a variety of other carbonaceous materials and methods. In early mass spectrometric studies, Drowart et al.[32] and Gupta et al.[37] formed small carbon cluster ions (C_n^+, n=1-3) by electron ionization of the corresponding neutral carbon clusters produced from the sublimation of graphite. In recent studies, carbon cluster ions were formed by laser desorption of diamond[-,], coal[43] and soot.[44] In addition, small carbon cluster ions have been produced by electron-impact ionization of suitable gas molecules as well. For example, Giles et al.[45] used benzene as a precursor and produced carbon cluster cations with n = 4-6 to study their reactivity with H_2 and CO. In a study by Dibeler et al.[46], cyanogen precursors were used to produce small carbon clusters, and the IP's of these species were determined. Results from that study are also compared to IP's bracketed in this study in Table 3. The IP's determined by Dibeler et al.[46] for carbon clusters (C_n,n=3,5,6) are somewhat in agreement with the IP's bracketed in this study.

Ionization potentials bracketed in this study are expected to be adiabatic[19] and they agree very well with all previous experimental adiabatic IP's.[32,41,46] Table 3 shows that the IP's of C_3, C_4 and C_5 agree somewhat and the IP of C_6 agrees very well with earlier theoretical adiabatic IP's.[38-40] Agreement with both experimental and theoretical IP's determined previously is much poorer.[18,36-37]

c) Side Reactions:

Several interesting side reactions were observed in addition to the charge-transfer reactions. These side reactions caused some difficulties in bracketing the IP's, but they gave some insight into the reactivity of the carbon clusters. Some of these ion-molecule reactions are given in Table 4. As shown in Figure 3a, during the reaction between C_3^+ and N_2O, several ion-molecule reactions were observed. The continuous ejection capability of the FTICR mass spectrometer was used in these reactions to ensure that charge-transfer was occurring in these reactions in a straightforward manner, rather than by some multiple reaction pathway. First, C_3O^+ was continuously ejected during the charge-transfer reaction time and O_2^+, NO^+, N_2O^+ and C_3^+ were monitored. Similarly, NO^+ and O_2^+ were continuously ejected and the reaction was repeated. These separate runs showed exponentially decaying intensity for C_3^+ and increasing intensity for N_2O^+, indicating that charge-transfer was occurring in a straightforward manner. When C_3O^+ was ejected continuously, $C_3O_2^+$ was not observed as one of the products. This suggests that $C_3O_2^+$ is formed by a step-wise reaction from C_3O^+. Since C_4^+, C_5^+ and C_6^+ did not undergo charge-transfer with N_2O, other reactions of these ions were not as difficult to study as those between C_3^+ and N_2O. During the reaction of C_5^+ with N_2O, C_5O^+ was formed as a primary product and $C_5O_2^+$ was formed as a secondary product. The even-numbered carbon cluster cations (4 and 6) underwent step-wise reaction with N_2O and formed $C_{n-1}O^+$ and $C_{n-1}O_2^+$.

No charge-transfer was observed between any of the four carbon cluster ions investigated in this study and CO_2. Initially, CO_2 reactions were carried out at 3.0×10^{-8}

Torr of CO_2; at this pressure the odd-numbered cluster ions formed C_nO^+ and $C_nO_2^+$ and the even-numbered cluster ions formed $C_{n-1}O^+$ and $C_{n-1}O_2^+$ at a slower rate than the reaction between C_n^+ and N_2O. However, when the pressure of CO_2 was increased to 1.0×10^{-7} Torr to ensure that charge-transfer was not occurring, the even-numbered cluster ions formed C_nO^+ and $C_nO_2^+$ in addition to forming $C_{n-1}O^+$ and $C_{n-1}O_2^+$. We also observed that the C_nH^+ formed by reaction with background water during the thermalizing time reacted further with N_2O or CO_2 during the charge-transfer reaction time to form OC_nH^+.

Comparison of C_n^+/CO_2 and C_n^+/N_2O reactions indicates that the C_n^+/CO_2 reaction is slower than the C_n^+/N_2O reaction. This difference in reaction rates of CO_2 and N_2O with C_n^+ is due to the difference in oxygen bond dissociation energy of CO_2 and N_2O. In a study by Kappes et al.[47] of the $M^+ + YO \longrightarrow MO^+ + Y$ reaction, several atomic metal cations, M^+, were formed by laser desorption in the presence of various oxidants, YO (O_3, N_2O, O_2, CO_2 SO_2, NO), and oxygen transfer was found to be dependent on oxygen bond dissociation energy. The same trend was observed in the present study, in which the oxygen bond dissociation energy (YO $\longrightarrow$ Y + O, where Y is N_2 or CO) of N_2O is 87 kcal/mol lower than that of CO_2.

Ion-molecule reactions between laser-generated carbon cluster cations and either D_2 or O_2 were studied by McElvany et al.[20] In that study, C_n^+ reacted with O_2 to form C_nO^+, C_{n-1}^+ and C_{n-2}^+ as the primary ion-molecule reaction products. The primary ion-molecule reaction products were observed to further react with O_2 to form $C_nO_2^+$, $C_{n-1}O^+$ and $C_{n-2}O^+$ as the secondary products. Secondary ion-molecule reaction products were

also observed to form at a higher rate for the odd-numbered clusters than for the even-numbered clusters. A similar trend and products were observed in our study for the reactions with N_2O and CO_2, except that the formation of C_{n-1}^+, C_{n-2}^+ and $C_{n-2}O^+$ was not detected.

Bernholc et al.[8] and McElvany et al.[20] have predicted that carbon cluster cations with fewer than 10 atoms are most stable in a linear configuration with reactive carbene sites at both ends of the chains. During the reaction of C_n^+ with N_2O and CO_2, C_nO^+ is formed, presumably with a double bond between the oxygen atom and one of the terminal carbons, and N_2 and CO are the respective neutral products. During the formation of the secondary product $C_nO_2^+$, as suggested by McElvany et al[20], the positive charge is delocalized onto the remaining terminal carbon of C_nO^+ for the odd-numbered carbon clusters while for the even-numbered clusters the positive charge is delocalized onto the n-1 carbon atom. Thus, the formation of $C_nO_2^+$ is preferentially favored for the odd-numbered carbon clusters, because of the positive terminal reaction site.

All carbon cluster cations were observed to react with background water, forming C_nH^+ rapidly. The reaction of carbon cluster cations with hydrogen has been studied previously.[22,45,46] Our results are generally consistent with findings in these previous studies. It is interesting to compare the results for the reactions of small carbon cluster cations with background water to those reported for reaction with D_2[20] and HCN.[22] The C_nD^+/D_2 reactions and the C_nH^+/HCN reactions both showed even/odd alternation in their reactivity, with the even-numbered carbon cluster cations more reactive than the

odd-numbered cluster ions. A similar even/odd alternation is observed in our C_nH^+/H_2O reactions.

These side reactions indicate that even and odd-numbered clusters react differently. In addition, during the reactions with N_2O or CO_2, carbon cluster ions were observed to form sequentially C_nO^+ and then $C_nO_2^+$, which did not undergo further reactions. Similarly, if C_nH^+ formed due to background water was not ejected from the cell, C_nH^+ was observed to react with N_2O or CO_2 to form OC_nH^+, and this OC_nH^+ then did not undergo further reactions. These observations suggest that these ion-molecule reactions may be occurring at two carbene ends of the linear carbon cluster ions.

CONCLUSIONS

Ionization potentials of small carbon clusters (C_n, n=3-6) have been bracketed successfully using a charge-transfer bracketing technique and FTICR mass spectrometry. The IP's determined in this study have smaller uncertainties than the literature values and agree well with adiabatic IP's available in literature. No evidence for structural isomers of small carbon clusters was observed. During these charge-transfer studies, several side reactions were observed with the charge-transfer reference compounds. These ion-molecule reactions showed an even/odd alternation in cluster ion reactivity and suggest that these reactions may be occurring at carbene ends of linear carbon chains.

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Table 1. Charge transfer reference compounds used in this study and their IP's

Reference compound	Ionization Potential[19]
Krypton	13.997
Carbon dioxide	13.77
Sulfuryl fluoride	13.04
Nitrous oxide	12.89
Freon 13	12.39
Sulfur dioxide	12.32
Acetonitrile	12.19
Xenon	12.13
PF_3	11.40
Acetylene	11.39
1,4-Dicyanobenzene	10.10
1-Fluoro-3-nitrobenzene	9.88
4-Nitrotoluene	9.52
3-Nitrotoluene	9.48
Benzene	9.25

Table 2. Results from reaction of carbon cluster cations with charge transfer neutrals.

Neutral	C_3^+	C_4^+	C_5^+	C_6^+
Krypton	N	N	N	
Carbon dioxide	N	N	N	
Sulfuryl fluoride	N	N	N	
Nitrous oxide	Y	N	N	N
Freon 13	Y		N	
Sulfur dioxide	Y		N	
Acetonitrile	Y	Y	Y	
Xenon	Y	Y	Y	
PF_3	Y	Y	Y	
Acetylene	Y	Y	Y	
1,4-Dicyanobenzene				N
1-fluoro-3-nitrobenzene				N
4-Nitrotoluene				Y
3-Nitrotoluene				Y
Benzene	Y	Y	Y	Y

N = Charge transfer between the cation and the charge transfer agent was not observed.
Y = Charge transfer was observed.

Table 3. Comparison of experimental and theoretical IP's of $C_3 - C_6$

C_n	This work	aIP(exp.)	aIP(theory)	vIP(exp.)	vIP(theory)
C_3	12.97±0.1	12.6±0.6[a,a] 12.1±0.3[b] <14.0[k,j] <13.6[k,j] 14.4[k,j]	12.7[c] 12.95[d] 11.4[e]	9.98-11.61[g,f] 11.1±0.5[h]	12.90[i,g] 11.5[i]
C_4	12.54±0.35	12.6[a]	10.58[e]	9.98-11.61[f]	11.39[g]
C_5	12.26±0.1	12.5±0.1[a] 12.7±0.5[j]	10.7[e]	9.98-11.61[f]	11.07[g]
C_6	9.70±0.2	9.6±0.3[k] 12.5±0.3[j]	9.8[e]	9.98-12.84[f]	10.41[g]

- reference 32
- reference 41
- reference 39
- reference 40
- reference 38
- reference 18
- These values were cited as personal communications in reference 18.
- reference 37
- reference 36
- reference 46
- reference 23

a b c d e f g h i j k

Table 4. Ion-molecule reactions of carbon clusters with charge-transfer reference compounds

C_n^+	CTRC	Reaction and products		
C_3^+	N_2O	$C_3^+ + N_2O$	------>	$C_3O^+ + N_2$
		$C_3O^+ + N_2O$	------>	$C_3O_2^+ + N_2^*$
		$N_2O^+ + N_2O$	------>	$O_2^+ + 2N_2$
		$N_2O^+ + N_2O$	------>	$NO^+ + NO + N_2$
	CO_2	$C_3^+ + CO_2$	------>	$C_3O^+ + CO$
		$C_3O^+ + CO_2$	------>	$C_3O_2^+ + CO^*$
	H_2O	$C_3^+ + H_2O$	------>	$C_3H^+ + OH$
C_4^+	N_2O	$C_4^+ + N_2O$	------>	$C_3O^+ + CN_2$
		$C_3O^+ + N_2O$	------>	$C_3O_2^+ + N_2^*$
	CO_2	$C_4^+ + CO_2$	------>	$C_4O^+ + CO$
		$C_4O^+ + CO_2$	------>	$C_4O_2^+ + CO^*$
	H_2O	$C_4^+ + H_2O$	------>	$C_4H^+ + OH$
C_5^+	N_2O	$C_5^+ + N_2O$	------>	$C_5O^+ + N_2$
		$C_5O^+ + N_2O$	------>	$C_5O_2^+ + N_2^*$
	CO_2	$C_5^+ + CO_2$	------>	$C_5O^+ + CO$
		$C_5O^+ + CO_2$	------>	$C_5O_2^+ + CO^*$
	H_2O	$C_5^+ + H_2O$	------>	$C_5H^+ + OH$
C_6^+	N_2O	$C_6^+ + N_2O$	------>	$C_5O^+ + CN_2$
		$C_5O^+ + N_2O$	------>	$C_5O_2^+ + N_2^*$
	CO_2	$C_6^+ + CO_2$	------>	$C_6O^+ + CO$
		$C_6O^+ + CO_2$	------>	$C_6O_2^+ + CO^*$
	H_2O	$C_6^+ + H_2O$	------>	$C_6H^+ + OH$

Where   * = step-wise reaction
             CTRC = charge-transfer reference compound

<u>Figure Captions:</u>

Figure 1. Mass spectra of carbon cations observed following laser vaporization of a graphite plug by 1064 nm excitation from a Nd:YAG laser with (a) 5 mJ/pulse and (b) 15 mJ/pulse.

Figure 2. Ion intensity vs. time for the reaction of C_3^+ with Xenon.

Figure 3. Ion intensity vs. time for reaction of (a) C_3^+, (b) C_4^+, and (c) C_5^+ with N_2O.
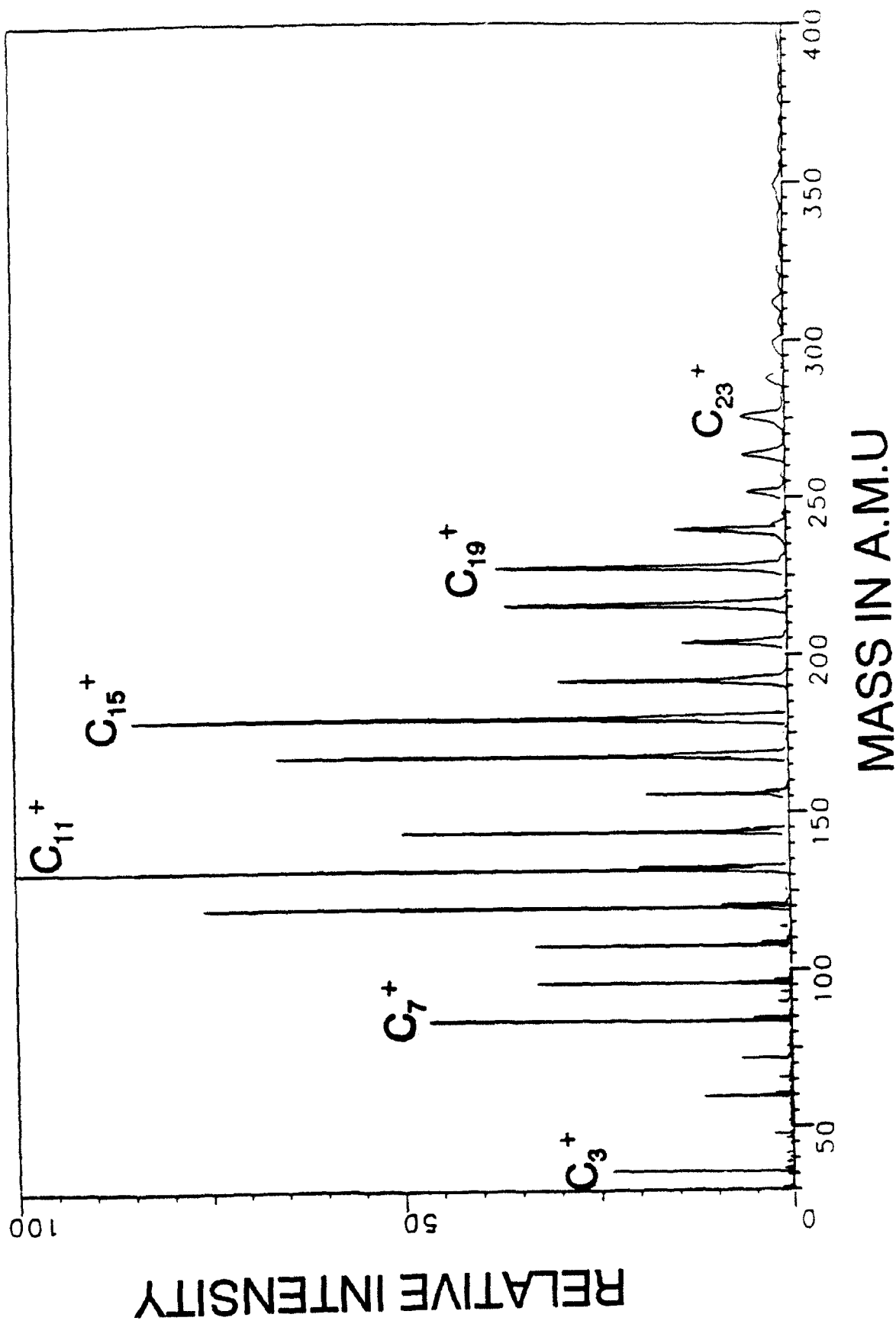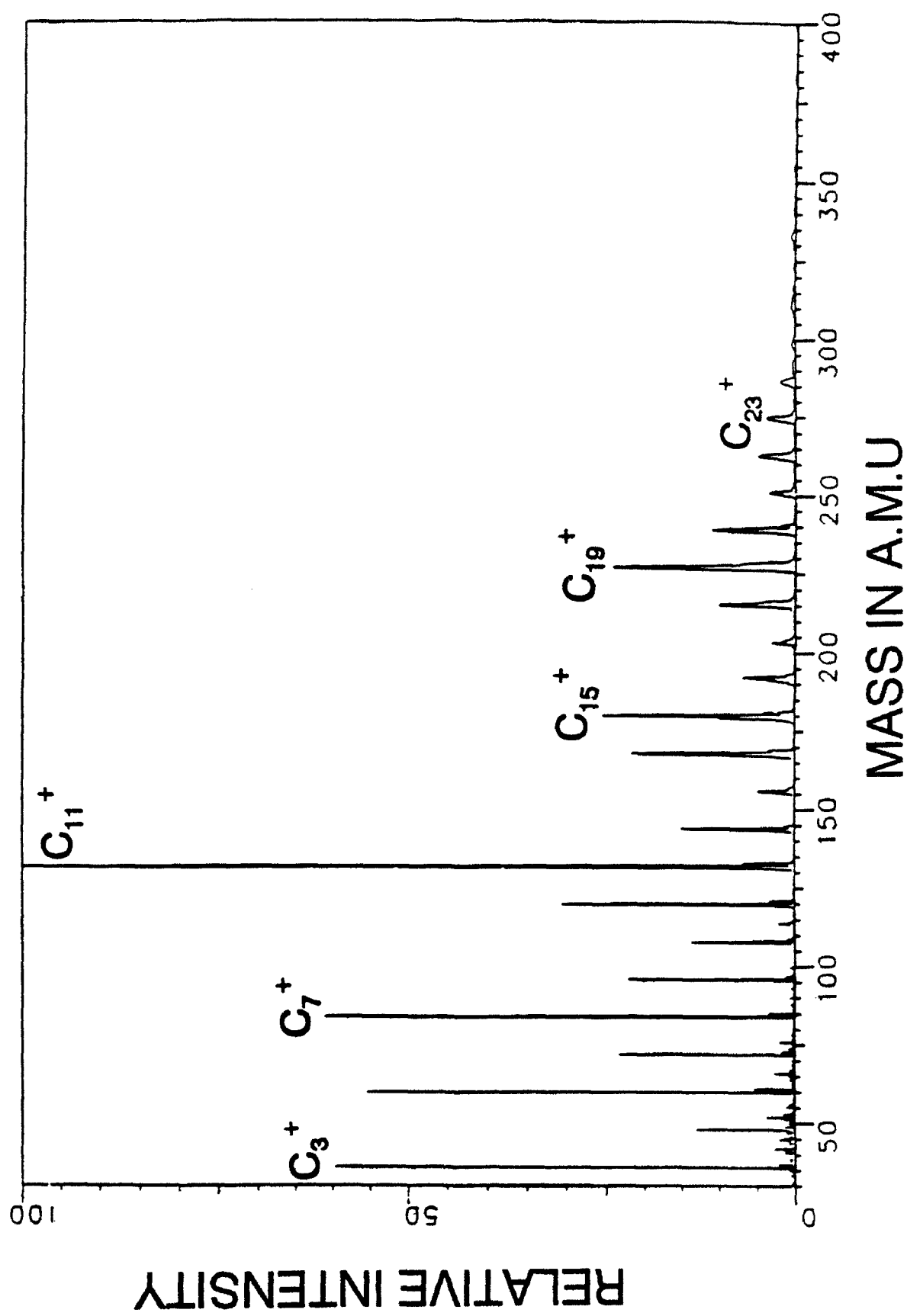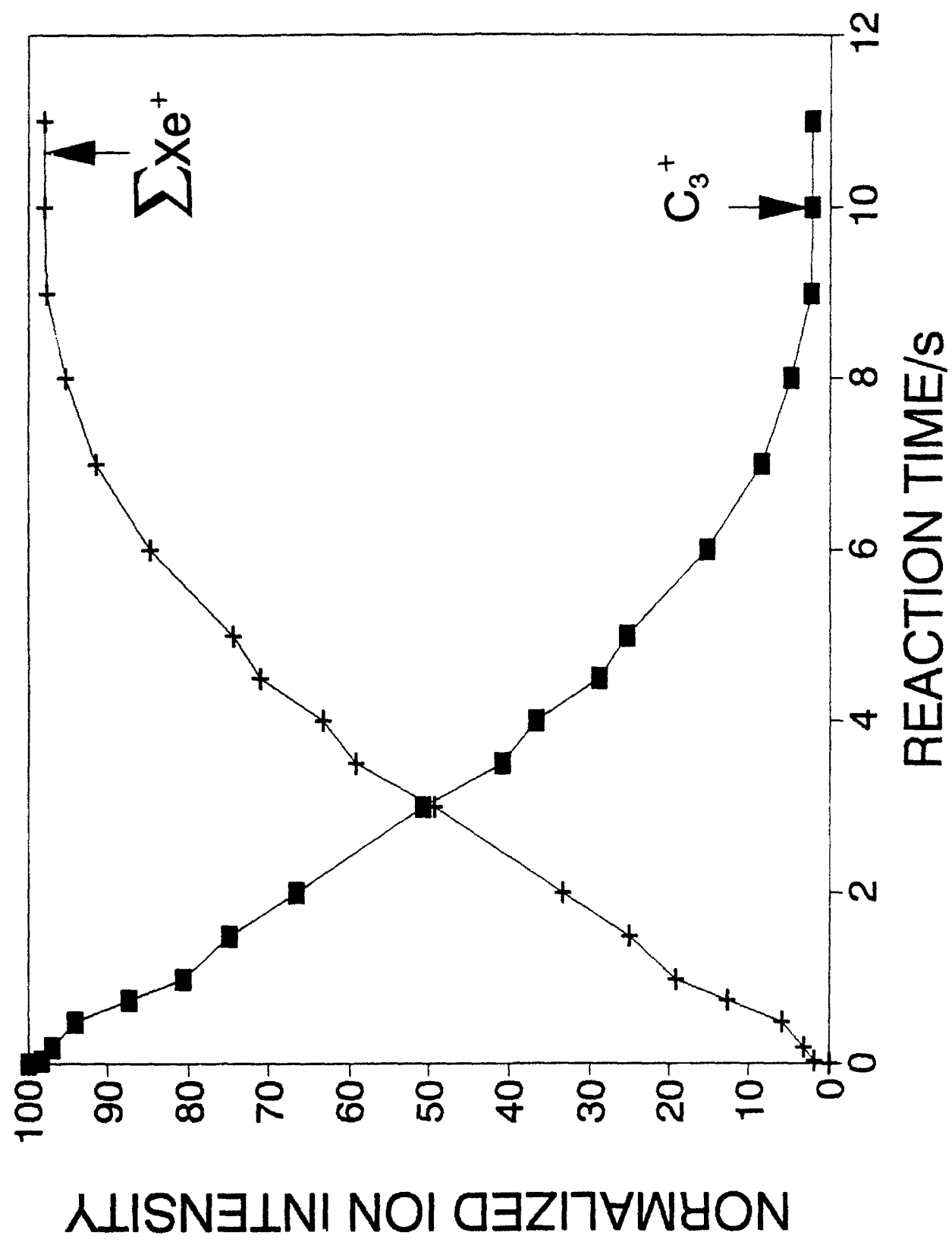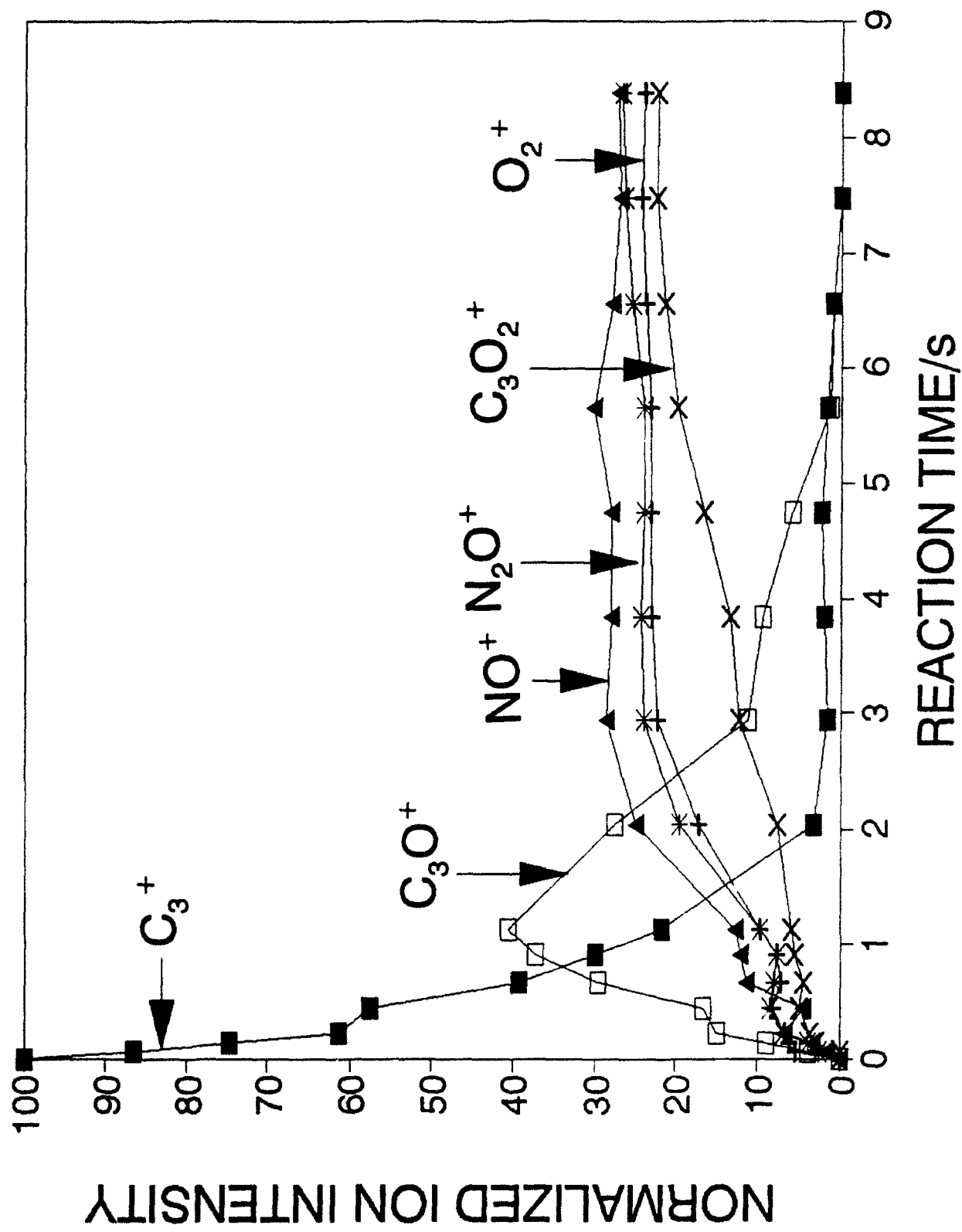
Fig 1a

Fig 1b

Fig 2

NORMALIZED ION INTENSITY vs REACTION TIME/s

$\sum Xe^+$

C_3^+

Fig 3b

REACTION TIME/s

NORMALIZED ION INTENSITY

C_4^+

C_3O^+

$C_3O_2^+$

N_2O^+

Fig. 3c